

Empirical Force-Field and *Ab Initio* Calculations on Delocalized Open Chain Cations

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ABSTRACT

Force-field calculations are reported for large delocalized cations. The results for the geometries, heats of formation, and π -electron densities agree well with MP2(full)/6-31G* *ab initio* calculations. Both methods give similar results for the distortion of the carbon skeletons of unsubstituted cations by hyperconjugating methyl groups. Because of the SCF treatment of π -interactions, the MMP2 force-field technique enables calculations of resonance energies in delocalized cations. The additional resonance stabilization produced by extending conjugation is directly related to the π -charge on the carbon at which a vinyl group is substituted. The good agreement of MMP2 results for nonbonded resonance effects in large delocalized cationic π -systems with *ab initio* data suggests that MMP2 can be used to study the influence of these interactions in cationic π -systems too large to be calculated by correlated *ab initio* methods.
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Introduction

Attempts to apply force-field methods to carbocations¹ date back to the early days of these techniques.² Since for a long time rate constants of solvolysis reactions were the only available data, early force-fields for carbocations concentrated on the calculation of strain energies, which can be correlated with solvolysis rate con-

stants.³⁻⁵ In contrast to these earlier parameterizations a new empirical force-field produces carbocation geometries quite well.⁶ Allinger's MMP2 method,⁷ which combines a quantum chemical SCF treatment of delocalized π -systems with an empirical force-field, was used for this parameterization. Geometries and π -electron densities of delocalized cations are described well by this new force-field program. Hyperconjugation effects, introduced by a quantum chemical term in the SCF routine of this program, are given reliably.

The allyl system proved to be ideal for studying the effects of hyperconjugation in delocalized car-

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bocations. Detailed investigations on allyl cations by correlated *ab initio* and force-field optimizations⁸ gave results that agreed well. MMP2 proved impressively the importance of 1–3 π -interactions in the allyl system and gave realistic heats of formations and resonance energies in the allyl system. These results encouraged us to study hyperconjugation, nonbonded resonance interactions, and heats of formation in larger delocalized systems by force-field calculations.

Larger polyenyl cations could be formed by protonation of polyenes, and are characterized by intensive colors^{9,10} due to extensive resonance effects and a shift of π – π^* electron transfers in the visible area. H-NMR spectra were able to characterize the polyenic character of such ions.¹¹ Protonation of polyenic alcohols proved to be an alternative method to form conjugated polyenyl cations.¹²

However, no X-ray data, ¹³C-NMR spectra, and vibrational spectra have been reported due to rapid rearrangements of these cations into cyclic isomers.¹³ The excellent coincidence of ¹³C chemical shifts obtained by GIAO-MP2 calculations¹⁴ on MP2(full)/6-31G* optimized geometries with experimental data in the allyl system¹⁵ showed that MP2(full)/6-31G* *ab initio* optimizations give realistic geometries. Therefore, we performed MP2(full)/6-31G* optimizations on larger delocalized polyenic cations, and compared the geometries with those at MMP2. Furthermore, heats of formation, resonance effects, and stabilization by nonbonded resonance interactions (e.g., 1–3 π -interactions) can be studied by MMP2 and compared with the allyl results.

Methods

All *ab initio* calculations used GAUSSIAN 92¹⁶ on Convex C220, Hewlett-Packard 9000-735 and Cray YMP-864 computers. The 6-31G*¹⁷ basis set was used for all optimizations, which were carried out using a second order Møller–Plesset correction for electron correlation based on the restricted Hartree–Fock wave function (RMP2).¹⁷ Optimization of delocalized cations with correlated *ab initio* methods is necessary for the correct calculation of both geometries and energies.¹⁹ The energies in the text refer to calculations on MP2(full)/6-31G* optimized geometries using a fourth order Møller–Plesset correction including single, double, triple, and quadruple excitations (MP4sdqtq)²⁰ for

molecules up to six carbon atoms and nine hydrogen atoms and a fourth order Møller–Plesset correction including single, double, and quadruple excitations (MP4sdqtq)²⁰ for larger molecules. All structures were characterized by frequency calculations at RHF/6-31G* on RHF/6-31G* optimized geometries.

The π -electron densities of delocalized cations and π -electron density matrix elements were obtained by applying the NPA analysis method²¹ on the structures optimized at MP2(full)/6-31G* using RHF/6-31G* wave functions.

The force-field calculations were performed with the MMP2 program²² adapted for the Convex C220/384 computer. The introduction of the cation parameters and the quantum mechanical changes in the SCF routine for the parameterization of the effects caused by hyperconjugation interactions has been described previously.⁶

1,3-Pentadien-5-yl System

PARENT CATION

MP2(full)/6-31G* and MMP2 optimizations showed that the (*E*, *E*)-1,3-pentadien-5-yl cation has C_{2v} symmetry (cf. Fig. 2). The energetically favored electrocyclization of this cation to the cyclopenten-3-yl cation has been predicted by *ab initio* calculations at MP2(full)/6-31G*.²³

The agreement for the carbon–carbon bond lengths suggests that Allinger's assumption that such bond lengths depend linearly on the π -bond orders also works well for carbocations. Both methods calculate a slightly reduced C1–C2–C3 angle, analogously to angle deviations observed in the allyl system,²⁴ and a large value for C2–C3–C4. This suggests a stabilizing nonbonded resonance effect between C1 and C3 and a destabilizing π -interaction between C2 and C4. These interactions influence the geometry and the stability of the π -system. The π -electron densities calculated by the two different methods agree well and give values consistent with resonance theory.

Nonbonded resonance effects, which have been predicted for the allyl system three decades ago,²⁵ can be studied easily for delocalized cations, because the nonbonded resonance integrals can be introduced optionally. Comparison of MMP2 π -energies obtained with and without nonbonded resonance integrals suggests a nonbonded resonance stabilization of 12.6 kcal/mol, larger than that found for the allyl cation (9.5 kcal/mol; cf. ref. 8).

A comparison of the products of resonance integrals and π -bond orders shows strong stabilizing nonbonded resonance effects between C1 and C3 and between C3 and C5 and moderate destabilizing π -interactions between C2 and C4. The destabilizing nonbonded resonance interactions between atoms C1–C4 and C1–C5 are of little importance because of the large distances involved (C1–C4: MMP2 3.730 Å, MP2(full)/6-31G* 3.712 Å, C1–C5: MMP2 4.772 Å, MP2(full)/6-31G* 4.781 Å). MMP2 gives a stabilization effect of 14.5 kcal/mol by exclusive calculation of the nonbonded resonance integrals C1–C3 and C3–C5. This strong stabilization is slightly weakened by the π -interactions between C2–C4, C1–C4, and C1–C5. Figure 1 compares the off-diagonal π -density matrix elements given by MMP2 and MP2(full)/6-31G*.

Analogously to the allyl cation we calculated the resonance energy of the 1,3-pentadien-5-yl cation by the force-field method. Table I lists MMP2 π -energies for some delocalized cations and unsaturated neutral molecules.

The 1,3-pentadien-5-yl cation can be regarded as a methyl cation substituted by two vinyl groups. Consequently, the resonance energy, E_{res} , of this cation can be calculated by:

$$\begin{aligned} E_{\text{res}} &= E_{\pi}(\text{1,3-pentadien-5-yl cation}) \\ &\quad - 2 \cdot E_{\pi}(\text{ethene}) \\ &= -79.4 \text{ kcal/mol} \end{aligned} \quad (1)$$

The value of -79.4 kcal/mol is evidently higher than the resonance energy of the allyl cation (-53.2 kcal/mol) because of more extensive charge delocalization. This effective resonance stabilization has already been predicted by *ab initio* calculations²⁶

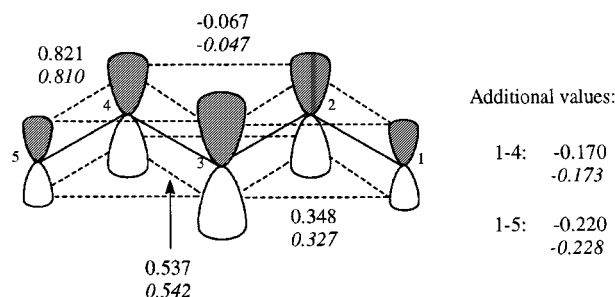


FIGURE 1. Off-diagonal π -density matrix elements as a measure for π -bond orders of the 1,3-pentadien-5-yl cation at MMP2 and MP2(full)/6-31G* [*italic*: values at MP2(full)/6-31G*].

based on isodesmic equations suggested by Apeloig and Schleyer.²⁷

The stabilization energy of a positive charge by a butadienyl-group $E_{\text{stab}}(\text{1,3-pentadien-5-yl cation})$ can be calculated analogously by:

$$\begin{aligned} E_{\text{stab}}(\text{1,3-pentadien-5-yl cation}) &= E_{\pi}(\text{1,3-pentadien-5-yl cation}) \\ &\quad - E_{\pi}(\text{1,3-butadiene}) \\ &= -72.6 \text{ kcal/mol} \end{aligned} \quad (2)$$

This value is significantly larger than that found for a vinyl group, again because of a more effective stabilization of the positive charge. The value of E_{stab} is moderately lower than the complete resonance energy of the 1,3-pentadien-5-yl cation, since this value does not include the resonance energy of 1,3-butadiene [-6.7 kcal/mol ($E_{\pi}(\text{1,3-butadiene}) - 2 \cdot E_{\pi}(\text{ethene})$)].

Finally, the 1,3-pentadien-5-yl cation can be regarded as an allyl cation stabilized by one vinyl group. The stabilization energy, $E_{\text{stab}}(\text{vinyl})$, for this variation can be calculated by:



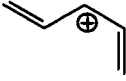

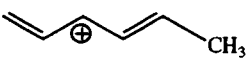
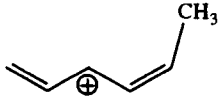
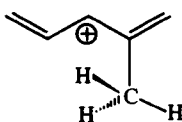
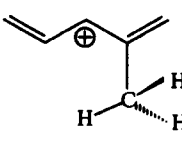
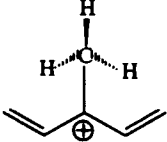
$$\begin{aligned} E_{\text{stab}}(\text{vinyl}) &= E_{\pi}(\text{1,3-pentadien-5-yl cation}) \\ &\quad - E_{\pi}(\text{allyl cation}) - E_{\pi}(\text{ethene}) \\ &= -26.1 \text{ kcal/mol} \end{aligned} \quad (3)$$

This stabilization energy is smaller than the resonance energy of the allyl cation, which is identical to the stabilization energy of a π -charge of 1.00 by a vinyl group, because a terminal allyl carbon only has a π -charge of 0.527 at MMP2 (cf. ref. 8).

The 1,3-pentadien-5-yl cation exhibits (*E*, *Z*)-isomerism. At MP4sdtq/6-31G*/MP2(full)/6-31G* and MMP2, the $C_{2v}(\text{E}, \text{E})$ -isomer is most stable. The $C_s(\text{E}, \text{Z})$ -isomer is 3.59 kcal/mol less stable than the (*E*, *E*)-isomer at MP4sdtq/6-31G*/MP2(full)/6-31G* (MMP2: 3.65 kcal/mol). MMP2 calculations suggest that this energy difference is mainly caused by steric energies [difference: 2.60 kcal/mol in favor of the (*E*, *E*)-isomer]. However, the π -energy of the (*E*, *E*)-isomer is 1.47 kcal/mol higher than that of the (*E*, *Z*)-isomer, a consequence of the stronger repulsion between the π -electrons in the (*E*, *Z*)-isomer. Figure 2 shows some geometric parameters of the (*E*, *Z*)-1,3-pentadien-5-yl cation at MP2(full)/6-31G* and MMP2 and that the atoms of the (*Z*)-vinyl group are involved in stronger repulsive


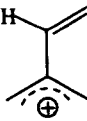
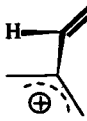
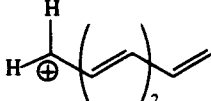
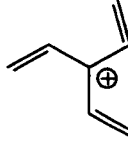
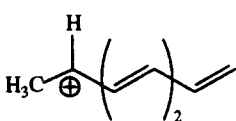
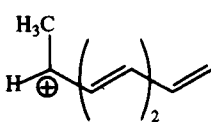
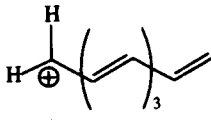
TABLE I.

Relative Energies (E_{rel}) at MP4sdtq / 6-31G* // MP2(full) / 6-31G*, MMP2 Relative Heats of Formation [$\Delta H_f(\text{rel})$],^a Nonbonded Resonance Stabilization Energies (E_{nobo}),^a Steric Energies (E_{st}),^a MMP2 π -Energies (E_{π}),^a and *Ab Initio* Energies at MP2(full) / 6-31G* // MP2(full) / 6-31G* (EMP2)^b and MP4sdtq / 6-31G* // MP2(full) / 6-31G* (EMP4)^b of Delocalized Open Chain Polyenyl Cations^c and Neutral Molecules.

Molecule	E_{rel} $\Delta H_f(\text{rel})$	E_{nobo}	E_{st}	E_{π}	EMP2 EMP4
	— —	9.5	−1.6	−108.8	−116.55762 −116.59211
	0.0 0.0	12.6	0.8	−190.6	−193.74350 −193.79432
	3.59 3.65	10.9	3.4	−189.1	−193.73742 −193.78861
	6.93 6.91	10.9	5.8	−189.9	−193.73288 −193.78328
	0.0 0.0	11.5	−5.1	−196.8	−232.93338 −232.99456
	2.79 0.89	11.1	−4.4	−196.1	−232.92867 −232.99011
	6.31 5.00	12.6	−2.5	−190.4	−232.92334 −232.98450
	7.61 5.76	12.8	−1.6	−190.3	−232.92116 −232.98242
	5.68 3.83	11.1	−1.5	−196.6	−232.92360 −232.98550

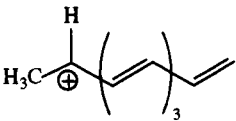
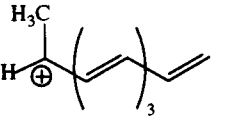




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TABLE I.
(continued)

Molecule	E_{rel} $\Delta H_f(rel)$	E_{nobo}	E_{st}	E_{π}	EMP2 EMP4
 C_1	0.0 0.0	9.9	-0.5	-174.4	-193.70690 -193.75879
 C_s planar	0.39 1.93	7.9	-0.8	-171.2	-193.70580 -193.75816
 C_s rotamer for the vinyl group rotation	2.61 1.96	9.8	2.4	-176.0	-193.70292 -193.75462
 C_2	0.0 0.0	14.0	-0.5	-262.8	-270.91537 -270.94075
	9.70 9.26	10.5	14.1	-260.0	-270.89802 -270.92529
 C_2	0.0 0.0	13.2	-6.3	-266.6	-310.10141 -310.13325
 C_2	2.61 1.06	12.8	-5.3	-265.9	-310.09722 -310.12809
 C_3	— —	14.7	-1.4	-330.2	-348.08054 -348.10823

(Continued on next page)

TABLE I.
(continued)

Molecule	E_{rel} $\Delta H_f(\text{rel})$	E_{nobo}	E_{st}	E_{π}	EMP2 EMP4
	0.0 0.0	14.1	-7.1	-333.0	-387.26432 -387.29731
	2.40 1.13	13.9	-6.0	-332.2	-387.26050 -387.29348
	— —	—	0.4	-55.6	— —
	— —	—	-2.5	-117.9	— —
	— —	—	-5.4	-181.2	— —
	— —	—	-8.2	-244.3	— —

^aValues in kilocalories per mole.^bValues in atomic units. For molecules containing more than six carbons, the MP4 ndq 16-31G* 11MP2(full)/16-31G* level is employed.^cWe could only perform MMP2 single-point calculations on the MP2(full)/6-31G* structure of the 2-vinylallyl cation rotamer, because MMP2 is not able to freeze four dihedral angles simultaneously.

interactions than in the (*E*)-vinyl group (cf. angles C1–C2–C3 and C3–C4–C5).

The C₂(*Z*, *Z*)-isomer (cf. Fig. 2) is 6.93 kcal/mol less stable than the (*E*, *E*)-isomer at MP4sdtq/6-31G*//MP2(full)/6-31G* (MMP2: 7.9 kcal/mol). The large strain energy of this isomer is reduced by distorting the π -system out of planarity. MMP2 computes a slightly lower distortion of the π -system out of planarity; as a consequence, the angle of the three central carbons is larger at MMP2 [MP2(full)/6-31G*: 123.0°; MMP2: 126.6°]. The main reasons for the instability of the (*Z*, *Z*)-isomer compared with the (*E*, *E*)-isomer are steric (5.0 kcal/mol). Torsional energies are most important, the Van der Waals and bending interactions also favor the (*E*, *E*)-isomer slightly. The remaining energy difference is a consequence of different SCF energies for the two π -systems, caused by distortion of the (*Z*, *Z*) π -system out of planarity.

Table I lists the *ab initio* energies and the energy differences of the three isomers at MP4sdtq/6-31G*//MP2(full)/6-31G* and MMP2.

SUBSTITUTION BY ONE METHYL GROUP

The C_s 1-methyl-1,3-pentadien-5-yl cation, for which rearrangements to cyclopenten-3-yl derivatives have long been known experimentally,²⁸ has one C–H bond of the methyl group eclipsed with the π -system analogously to the 1-methylallyl cation (cf. Fig. 2).²⁹ MMP2 finds a significantly lower π -electron density for the trigonal carbon attached to the methyl group than MP2(full)/6-31G* because MMP2 is not able to reproduce the electron donor effects of the hyperconjugating C–H bonds since it does not include σ -electrons. Hyperconjugation with the methyl group leads to an elongation of the bonds C2–C3 and C4–C5 com-

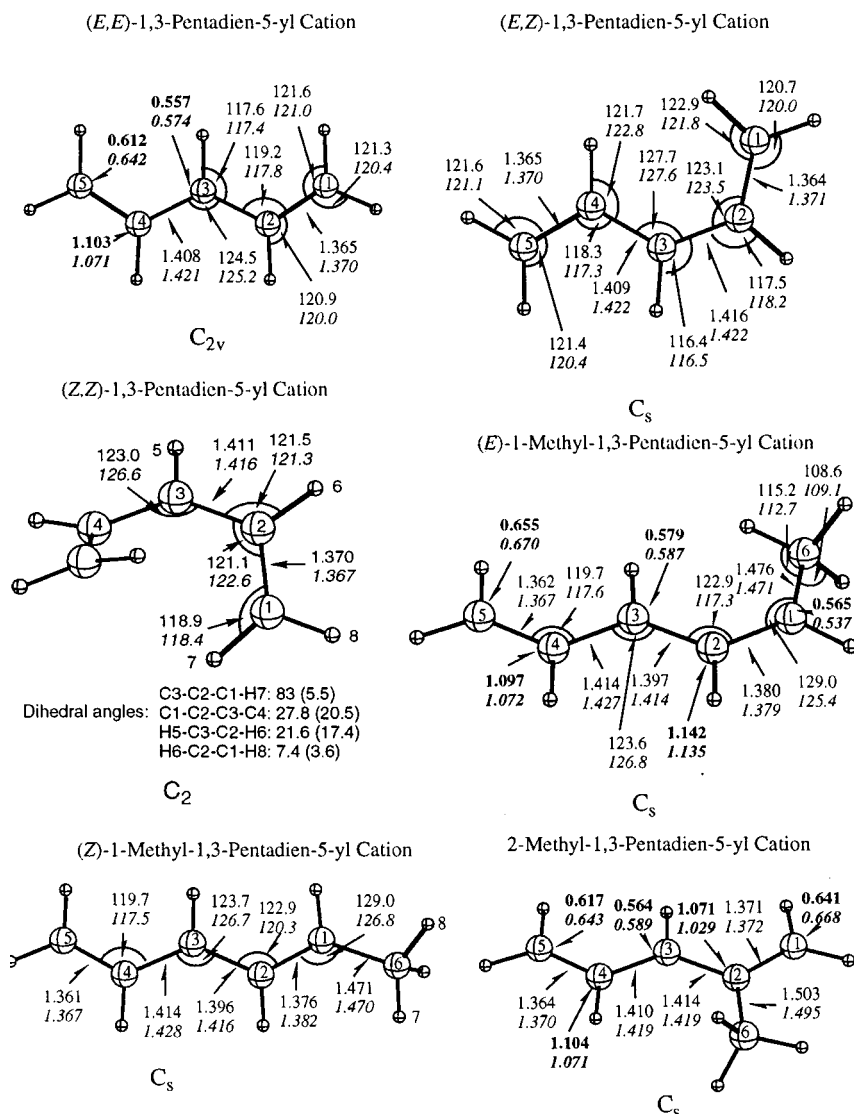


FIGURE 2. Geometry parameters^a and π -electron densities^{b,c} of open chain polyenyl cations at MP2(full)/6-31G* and at MMP2^d.

pared with the unsubstituted 1,3-pentadien-5-yl cation (cf. Fig. 2) because of the reduced π -bond orders of these bonds and, consequently, to a shortening of the bonds C3–C4 and C5–C6 due to an increase of the π -bond orders. The two methods give comparable changes in geometry of the 1,3-pentadien-5-yl cation caused by the methyl group. The C1–C6–H8 angle is decreased because of hyperconjugation of the C6–H8 bond.

The 1-methyl-1,3-pentadien-5-yl cation can exist as both an (*E*)- and (*Z*)-isomer. The (*Z*)-isomer is calculated to be 2.79 kcal/mol less stable than the (*E*)-isomer at MP4sdtq/6-31G*//MP2(full)/6-

31G* [MMP2 favors the (*E*)-isomer by 0.89 kcal/mol]. This energy difference is mainly caused by steric energies (torsional energies play the major part). Figure 2 shows interesting geometric features of the (*Z*)-isomer at MP2(full)/6-31G* and MMP2.

The 3-methyl-1,3-pentadien-5-yl cation has C_s symmetry with one C–H bond of the methyl group perpendicular to the π -system according to both MP2(full)/6-31G* and MMP2 (cf. Fig. 2). The methyl group attached to the central pentadienyl carbons leads to an elongation of the two central pentadienyl C–C bonds and, consequently, to a

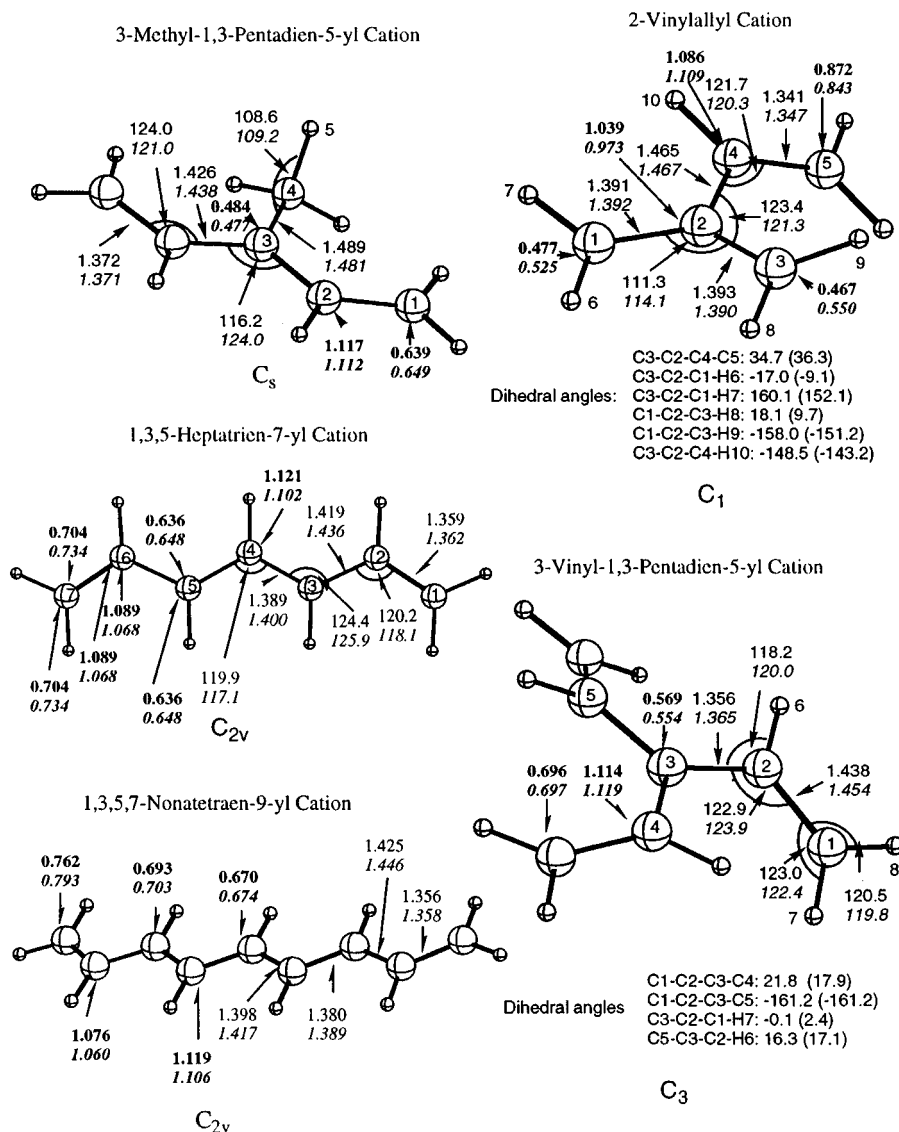


FIGURE 2. (Continued)

moderate shortening of the two terminal pentadienyl C–C bonds (cf. Fig. 2). Furthermore, a moderate deviation of the C3–C4–H5 angle from tetrahedral as a consequence of the strong hyperconjugation of the C4–H5 bond can be seen. However, this effect is moderate compared with the classical ethyl and 1-methylallyl cations.

The C_s 2-methyl-1,3-pentadien-5-yl cation has one methyl C–H bond eclipsed with the terminal pentadienyl carbon according to both MP2(full)/6-31G* and MMP2 (cf. Fig. 2). The attached methyl group influences the pentadienyl C–C bond lengths only minimally due to a weak hyperconjugation effect. The π -electron density of the trigonal

carbon attached to the methyl group is slightly reduced resulting in a moderate increase of the π -electron densities of the carbons C1 and C3 (cf. Fig. 2).

The conformer of the 2-methyl-1,3-pentadien-5-yl cation with C_s symmetry and one methyl C–H bond eclipsed with the central pentadienyl carbon is found to be a transition state for the rotation of the methyl group at MP2(full)/6-31G* and MMP2. The minimum structure is favored over the transition state by 1.30 kcal/mol at MP4sdtq/6-31G*//MP2(full)/6-31G* (MMP2: 0.76 kcal/mol). According to MMP2 this energy difference is mainly caused by larger angle strain as a conse-

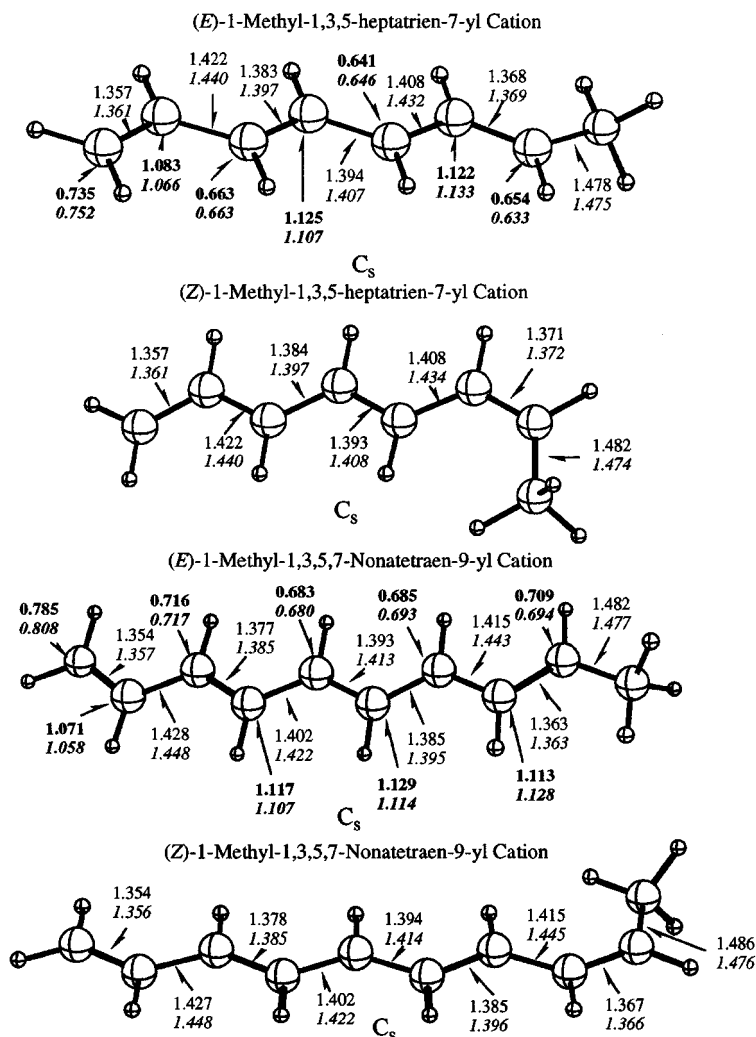
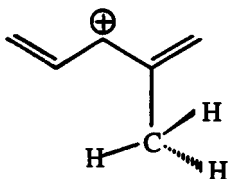


FIGURE 2. (Continued)

quence of the enlargement of the angle of the three central pentadienyl carbons [MMP2: 126.8°; MP2(full)/6-31G*: 127.1°].



We now compare relative energies of the methyl-1,3-pentadien-5-yl cation isomers at MP4sdtq/6-31G**//MP2(full)/6-31G*, their MMP2 relative heats of formation, and the reasons for the different stabilities of the isomers according to the MMP2 calculations. Table I lists the results. The two methods compute the same energetic sequence of the different isomers. MMP2 gives lower

energy differences between the isomers than the *ab initio* calculations. We were surprised to find the 3-methyl-1,3-pentadien-5-yl cation to be less stable than the 1-methyl-1,3-pentadien-5-yl cation isomers. The MMP2 data show that steric energies are the main reason. However, MMP2 suggests that the 1-methyl-1,3-pentadien-5-yl cation isomers have a slightly better π -energy than the 3-methyl-1,3-pentadien-5-yl cation. The 2-methyl-1,3-pentadien-5-yl cation is less stable than the other isomers as a result of the very low hyperconjugative stabilization of the methyl group.

Results for nonbonded resonance effects in alkylated allyl cations showed that hyperconjugation interactions reduce the importance of stabilizing nonbonded π -interactions (cf. ref. 8). However, hyperconjugation is of minor importance in the 1,3-pentadien-5-yl system because of better delo-

calization of the charge. Therefore, we expect little influence of hyperconjugation in the 1,3-pentadien-5-yl system, as confirmed by the force-field calculations. Table I lists the results.

The methyl group in the 1-methyl-1,3-pentadien-5-yl cation reduces nonbonded resonance stabilization by 1.1 kcal/mol. This reduction is lower than the value observed for the 1-methylallyl cation (reduction of the nonbonded resonance interaction compared with the unsubstituted allyl cation: 1.6 kcal/mol; cf. ref. 8). The reduction of nonbonded resonance stabilization by hyperconjugating methyl groups in the 3-methyl-1,3-pentadien-5-yl cation (1.5 kcal/mol) is the same magnitude as in the 1-methylallyl cation. This is because hyperconjugation in this cation reduces the magnitude of the two 1,3 π -interactions. The methyl group in the 2-methyl-1,3-pentadien-5-yl cation has no influence on these nonbonded resonance effects in the 1,3-pentadien-5-yl system because of its low hyperconjugation.

2-VINYLLALLYL CATION

The force-field and MP2(full)/6-31G* optimizations agree on C_1 symmetry for the 2-vinylallyl cation (cf. Fig. 2). We found a large distortion of the π -system out of planarity, similar to that in (Z)-1,3-butadiene [MMP2 finds a planar minimum for (Z)-1,3-butadiene; *ab initio* calculations at MP2(full)/6-31G* show C_2 symmetry and a twisting of the 1,3-butadiene vinyl groups of 37.9° towards each other]. MMP2 tends to a more moderate distortion of the *endo* hydrogens and to a larger distortion of the *exo* hydrogens out of planarity. Both methods calculate a significantly reduced allyl C–C–C angle [MP2(full)/6-31G*: 111.3°; MMP2: 114.1°], significantly smaller than that in the parent allyl cation [MP2(full)/6-31G*: 117.6°; MMP2: 118.6°]. We also performed MMP2 and MP2(full)/6-31G* calculations on the planar 2-vinylallyl cation and the rotamer of the 2-vinylallyl cation with a perpendicular conformation of the vinyl group toward the allyl system (cf. Table I).

The stabilization energy, E_{stab} , of the vinyl group attached to the central allyl carbon of the 2-vinylallyl cation can be calculated by:

$$E_{\text{stab}} = E_{\pi}(\text{2-vinylallyl cation}) - E_{\pi}(\text{allyl cation}) - E_{\pi}(\text{ethene}) \quad (4)$$

Eq. (4) gives a stabilization energy of –6.8 kcal/mol for the planar 2-vinylallyl cation. This is a consequence of the resonance effect of the vinyl

group with the allyl π -system and is similar to the resonance energy of 1,3-butadiene [$E_{\pi}(\text{1,3-butadiene}) - 2 \cdot E_{\pi}(\text{ethene}) = -6.7 \text{ kcal/mol}$]. However, we were surprised to find a more negative π -energy and a better vinyl stabilization effect for the perpendicular 2-vinylallyl cation (–11.6 kcal/mol). MMP2 shows a large stabilization effect by polarization of the vinyl π -electrons (π -electron densities: C4: 1.130; C5: 0.818). This polarization effect is superior to the resonance stabilization of the planar form. The nonbonded resonance energies of the 2-vinylallyl cation rotamers are at maximum in the C_1 minimum structure, but significantly lower in the planar form. The small allyl C–C–C angle of 114.1° [MP2(full)/6-31G*: 111.3°] is, to some extent, a consequence of steric repulsion caused by the vinyl group. The decrease of this angle is supported by the increasing nonbonded resonance stabilization that overcompensates the increasing angle strain. MMP2 and MP2(full)/6-31G* calculate a minimum allyl C–C–C angle for the C_1 structure and a larger value for the planar C_s structure [MMP2: 116.0°; MP2(full)/6-31G*: 112.9°]. MMP2 computes a minimum in the π -energy for the C_s structure with the perpendicular vinyl group. Why is this rotamer not the minimum structure of the 2-vinylallyl cation? The NBO analysis gives no answer. Therefore, we assumed that a repulsion of the vinyl σ -bond with the allyl π -electrons is the most probable reason for the high energy of the rotamer (repulsive interactions cannot be seen by the NBO analysis). MMP2 favors the C_1 structure due to a minimal steric energy (torsional energies play the major part) over the rotamer. The MMP2 heat of formation of the minimum is 19.03 kcal/mol higher than that of the isomeric 1,3-pentadien-5-yl cation [MP4sdtq/6-31G*//MP2(full)/6-31G*: 22.30 kcal/mol].

Larger Systems

UNMETHYLATED SYSTEMS

The 1,3,5-heptatrien-7-yl cation has C_{2v} symmetry at both MP2(full)/6-31G* and MMP2. The π -electron densities and the C–C bond lengths show an increasing delocalization of the charge compared with smaller delocalized cations (cf. Fig. 2). Allinger's assumption that C–C bond lengths depend linearly on the π -bond orders also works well for the 1,3,5-heptatrien-7-yl cation. These bond lengths are similar, because resonance effects are

at maximum in delocalized carbocations³⁰ and the π -charge is highly delocalized. Only the terminal C–C bonds show significant double bond character. Both methods give a large C2–C3–C4 angle.

Contributions of individual stabilizing and destabilizing nonbonded resonance effects to the total nonbonded resonance stabilization energy of 14.0 kcal/mol can be analyzed analogously to the 1,3-pentadien-5-yl cation (the data are available from Supplementary Material). MMP2 and MP2(full)/6-31G* off-diagonal π -density matrix elements agree well and show that the MMP2 nonbonded resonance energies are realistic.

The resonance energy, E_{res} , of the 1,3,5-heptatrien-7-yl cation, given by eq. (5), is higher than that of the 1,3-pentadien-5-yl cation (–79.4 kcal/mol) because of the additional vinyl group, which, however, is less effective than the terminal vinyl group in the 1,3-pentadien-5-yl cation:

$$\begin{aligned} E_{\text{res}} &= E_{\pi}(1,3,5\text{-heptatrien-7-yl cation}) \\ &\quad - 3 \cdot E_{\pi}(\text{ethene}) \\ &= -95.9 \text{ kcal/mol} \end{aligned} \quad (5)$$

The stabilization energy, $E_{\text{stab}}(\text{vinyl})$, of the terminal vinyl group, calculated by eq. (6), is lower than the stabilization effect of the terminal vinyl group in the 1,3-pentadien-5-yl cation (–26.1 kcal/mol) due to the smaller π -charge stabilized by the vinyl group:

$$\begin{aligned} E_{\text{stab}}(\text{vinyl}) &= E_{\pi}(1,3,5\text{-heptatrien-7-yl cation}) \\ &\quad - E_{\pi}(1,3\text{-pentadien-5-yl cation}) \\ &\quad - E_{\pi}(\text{ethene}) = -16.6 \text{ kcal/mol} \end{aligned} \quad (6)$$

The complete charge stabilization energy, $E_{\text{stab}}(1,3,5\text{-heptatrien-7-yl cation})$, given by eq. (7), shows that 1,3,5-hexatriene stabilizes the π -charge better than 1,3-butadiene (–72.6 kcal/mol). It is significantly lower than the complete resonance energy, E_{res} , because 1,3,5-hexatriene itself has a significant resonance energy [$E_{\pi}(1,3,5\text{-hexatriene}) - 3 \cdot E_{\pi}(\text{ethene}) = -14.4 \text{ kcal/mol}$]:

$$\begin{aligned} E_{\text{stab}}(1,3,5\text{-heptatrien-7-yl cation}) &= E_{\pi}(1,3,5\text{-heptatrien-7-yl cation}) \\ &\quad - E_{\pi}(1,3,5\text{-hexatriene}) \\ &= -81.6 \text{ kcal/mol} \end{aligned} \quad (7)$$

MP2(full)/6-31G* and MMP2 optimizations

show that the 3-vinyl-1,3-pentadien-5-yl cation has C_3 symmetry with a pronounced distortion of the π -system out of planarity (cf. Fig. 2). The three terminal vinyl groups have large double bond characters, while the C–C bonds of the atoms attached to the central carbon are longer than all C–C bonds of the isomeric 1,3,5-heptatrien-7-yl cation. These results may be a consequence of the slight distortion of the π -system out of planarity and a moderate localization of the π -charge at the central carbon (at MMP2 π -electron densities of the carbons attached to a terminal vinyl group: 1,3,5-heptatrien-7-yl cation: 0.648; 3-vinyl-1,3-pentadien-5-yl cation: 0.554).

The MMP2 π -energy is 2.7 kcal/mol higher than that of the 1,3,5-heptatrien-7-yl cation, although the π -charge stabilized by the third vinyl group attached to the central carbon is larger than that stabilized by a terminal vinyl group in the 1,3,5-heptatrien-7-yl cation. This is a consequence of the distortion of the π -system out of planarity. The steric energy of the 3-vinyl-1,3-pentadien-5-yl cation is higher than that of the 1,3,5-heptatrien-7-yl cation. Both effects cause the MMP2 heat of formation (230.0 kcal/mol) to be 9.3 kcal/mol higher [MP4sdq16-31G*//MP2(full)16-31G*: 9.7 kcal/mol] than that of the 1,3,5-heptatrien-7-yl cation (220.8 kcal/mol). The distortion of the 3-vinyl-1,3-pentadien-5-yl cation out of planarity causes a reduction of the importance of nonbonded resonance (3-vinyl-1,3-pentadien-5-yl cation: 10.5 kcal/mol; 1,3,5-heptatrien-7-yl cation: 14.0 kcal/mol).

The bond lengths of the C_{2v} 1,3,5,7-nonatetraen-9-yl cation show an increasing double bond character of the terminal C–C bonds as a result of the decreasing charge centered on the terminal carbons (cf. Fig. 2). Although the 1,3,5,7-nonatetraen-9-yl cation presents a significantly larger number of possibilities for nonbonded 1–3 π -interactions compared with the 1,3,5-heptatrien-7-yl cation, the MMP2 nonbonded resonance stabilization energy (14.7 kcal/mol) is only insignificantly higher than that of the 1,3,5-heptatrien-7-yl cation (14.0 kcal/mol), which is a consequence of the better delocalization of the π -charge and the smaller π -charges centered on the individual carbons.

Resonance energies in the 1,3,5,7-nonatetraen-9-yl cation can be computed analogously to the 1,3-pentadien-5-yl and 1,3,5-heptatrien-7-yl cations (cf. π -energies Table I). The results give a low charge stabilization energy of the terminal vinyl group (–11.8 kcal/mol) and a total resonance

energy in this delocalized π -system (-107.8 kcal/mol) that is moderately higher than that in the 1,3,5-heptatrien-7-yl cation (-95.9 kcal/mol).

1-METHYL-POLYENYL CATIONS

The (*E*)- and (*Z*)-isomers of the 1-methyl-1,3,5-heptatrienyl and 1-methyl-1,3,5,7-nonatetraen-9-yl cations show the decreasing influence of hyperconjugation interactions in large cationic π -systems. The (*E*)-1-methyl-1,3,5-heptatrien-7-yl cation is favored over the (*Z*)-isomer by 2.62 kcal/mol at MP4sdq/6-31G*//MP2(full)/6-31G* (MMP2: 1.06 kcal/mol). This energy difference is mainly caused by steric energies (Van der Waals repulsions play the major part). The corresponding energy difference in the 1-methyl-1,3,5,7-nonatetraen-9-yl cation is 2.40 kcal/mol in favor of the (*E*)-isomer at MP4sdq/6-31G*//MP2(full)/6-31G* (MMP2: 1.13 kcal/mol). The weak hyperconjugation interactions influence the strengths of nonbonded resonance stabilization effects only minimally in these cations according to MMP2 (1,3,5-heptatrien-7-yl cation: 14.0 kcal/mol; 1-methyl-1,3,5-heptatrien-7-yl cation: 13.2 kcal/mol; 1,3,5,7-nonatetraen-9-yl cation: 14.7 kcal/mol; 1-methyl-1,3,5,7-nonatetraen-9-yl cation: 14.1 kcal/mol).

Heats of Formation

With exception of the 1,3-pentadien-5-yl cation the heats of formation of the cations discussed in this article have not been determined experimentally. The MMP2 value for this cation (220.1 kcal/mol) agrees well with experiment (220 kcal/mol).³¹

The relative energies of isomeric allyl cations calculated by *ab initio* methods correspond excellently with the experimentally determined heats of formation of these isomers.⁸ This suggests that heats of formation of carbocations, which have not been determined experimentally, can be calculated by comparing their electronic energy at MP4/6-31G*//MP2(full)/6-31G* with that of isomers with experimentally determined heats of formation, and to add the energetic difference to the heat of formation of this isomer. Table II lists the MMP2 heats of formation for a number of delocalized carbocations, the heats of formation of these cations calculated by *ab initio* data, the reference cations for these calculations, the experimentally deter-

mined heats of formation of these reference cations, their *ab initio* energies at MP4sdq/6-31G*//MP2(full)/6-31G*, and the MMP2 heats of formation of some larger delocalized carbocations.

The heats of formation show the increasing inefficiency of hyperconjugation in large delocalized cations. The methyl group attached to a terminal carbon of the allyl cation reduces the heat of formation of the 1-methylallyl cation by 22.3 kcal/mol according to MMP2 (MMP2 heats of formation: allyl cation: 225.0 kcal/mol; 1-methylallyl cation: 202.7 kcal/mol; experimental values: allyl cation: 226 kcal/mol^{32,35,36}; 1-methylallyl cation: 202 kcal/mol^{33,35,36}). The methyl group attached to a terminal carbon of the 1,3-pentadien-5-yl cation reduces the heat of formation by 19.3 kcal/mol according to MMP2 (comparison of the heats of formation of the 1,3-pentadien-5-yl cation determined by experiment and the 1-methyl-1,3-pentadien-5-yl cation calculated by *ab initio* data gives a value of 15.3 kcal/mol). The corresponding values for larger delocalized systems are 16.1 kcal/mol (MMP2) and 16.2 kcal/mol (MP4sdq/6-31G*//MP2(full)/6-31G*) for the 1,3,5-heptatrien-7-yl system and 13.9 kcal/mol (MMP2) and 12.3 kcal/mol (MP4sdq/6-31G*//MP2(full)/6-31G*) for the 1,3,5,7-nonatetraen-9-yl system.

The MMP2 heats of formation of unsubstituted *all-trans* polyenyl cations containing up to seven carbons decrease with increasing chain length (methyl cation: 260.9 kcal/mol; experimental value: 261.3 kcal/mol³⁴⁻³⁶ allyl cation: 225.0 kcal/mol; experimental value: 226 kcal/mol; cf. ref. 6). The heat of formation of the 1,3-pentadien-5-yl cation (experimental value: 220 kcal/mol; MMP2: 220.1 kcal/mol) proves that the resonance energy of the terminal vinyl group overcompensates the positive contribution of the vinyl group to the heat of formation. However, this effect is small because of the significantly lower resonance energy of the terminal vinyl group. The resonance energy of the terminal vinyl group in the 1,3,5-heptatrien-7-yl cation approximately compensates its positive contribution to the heat of formation, and therefore, the heats of formation of the 1,3-pentadien-5-yl and 1,3,5-heptatrien-7-yl cations are similar. In larger *all-trans* polyenyl cations the resonance energies of the terminal vinyl groups decrease with increasing chain length, and therefore, the heats of formation of these cations increase with increasing chain length. Figure 3 shows the changes of the MMP2 heats of formation with increasing chain length graphically.

TABLE II.

Heats of Formation of Delocalized Carbocations Calculated by MMP2 [ΔH_f (MMP2)], Heats of Formation of These Cations Calculated by *Ab Initio* Data [ΔH_f (MP4)], Reference Cations for These Calculations, *Ab Initio* Energies at MP4sdq / 6-31G* // MP2(full) / 6-31G* (EMP4), and Experimental Heats of Formation^a [ΔH_f (exp)] of the Reference Cations.

Cation	ΔH_f (MMP2)	ΔH_f (MP4)	Reference cation	EMP4	ΔH_f (exp)
	200.8	204.7			
	205.8	208.5			
	204.7	207.5		-232.97900	191
	220.8	218.9			
	230.0	228.6		-270.98997	188
	204.7	202.7		-310.17792	174
	226.2	224.8		-384.17000	186

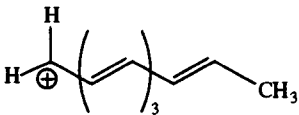
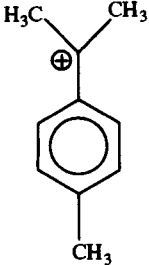
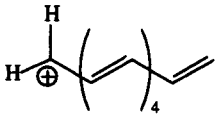
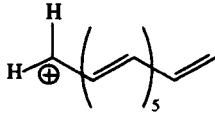
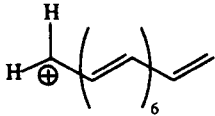
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Resonance Effects of Vinyl Groups

The resonance effects of the terminal vinyl groups in larger delocalized cations decrease with increasing chain length (cf. 1,3-pentadien-5-yl, 1,3,5-heptatrien-7-yl, and 1,3,5,7-nonatetraen-9-yl

cations) due to the increasing delocalization of the charge. We calculated the resonance energies of the terminal vinyl groups E_{res} (vinyl) of linear *all-trans* polyenyl cations poly(*n*) with *n* vinyl groups E_{res} (vinyl) = E_{π} (poly(*n*)) - E_{π} (poly(*n* - 1)) - E_{π} (ethene) and correlated the results with the π -charge stabilized by the terminal vinyl group

TABLE II.
(continued)

Cation	ΔH_f (MMP2)	ΔH_f (MP4)	Reference cation	EMP4	ΔH_f (exp)
	212.3	212.5		-387.35868	174
	234.1				
	243.7				
	254.4				

Heats of formation in kilocalories per mole, *ab initio* energies in atomic units.^aSee refs. 35 and 36.

[i.e., the π -charge of a terminal carbon of the linear *all-trans* polyenyl cation $\text{poly}(n - 1)$]. Table III lists and Figure 4 illustrates the results.

The resonance energy of a vinyl group depends linearly on the π -charge stabilized by the vinyl group. For small π -charges we observed significant deviations from this straight line. The reason for this deviation is the fact that the π -charge is not the only factor that influences the strengths of resonance energies, because small resonance energies also appear in neutral molecules (MMP2 calculates a resonance energy of -6.7 kcal/mol for 1,3-butadiene; cf. Table I). For small π -charges the observed graph leaves the straight line, and the calculated resonance energies are characteristic for neutral molecules (MMP2 resonance energy of the terminal vinyl group in 1,3,5,7-octatetraene: 7.5 kcal/mol; MMP2 resonance energy of a terminal vinyl group in a linear *all-trans* polyene with 20

carbons: 7.1 kcal/mol; the reason for the moderate smaller resonance energies of terminal vinyl groups in large cations compared with neutral polyenes is discussed in the next section).

Nonbonded Resonance Effects in Large Delocalized Cations

The MMP2 calculations on the allyl, 1,3-pentadien-5-yl, 1,3,5-heptatrien-7-yl, and 1,3,5,7-nona-tetraen-9-yl cations showed an increasing nonbonded resonance stabilization energy due to the increasing possibilities for 1-3 interactions. The example of the 3-vinyl-1,3-pentadien-5-yl cation proves that side-attached vinyl groups do not lead to an increase of nonbonded π -interactions. The nonbonded π -stabilization energy of the 3-vinyl-1,3-pentadien-5-yl cation (10.5 kcal/mol) is lower

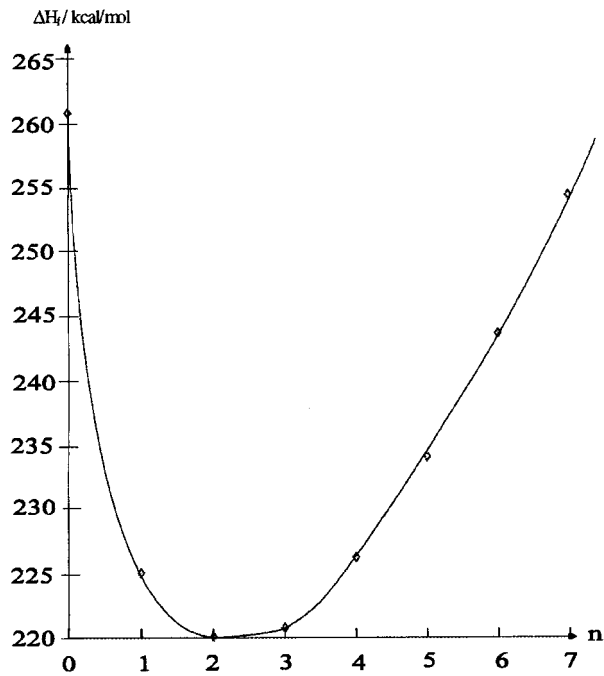


FIGURE 3. Dependence of the heats of formation of linear *all-trans* polyenyl cations ${}^+\text{CH}_2-(\text{CH}=\text{CH})_n-\text{H}$ on the chain length n .

than that of the smaller 1,3-pentadien-5-yl cation (12.6 kcal/mol) as a result of the distortion of the π -system out of planarity. However, the linear *all-trans* polyenyl cations are planar, and therefore, the question arose, whether the increasing number of possible 1–3 interactions is overcompensated by the fact that the individual carbons in larger cations have decreasing π -charges and, consequently, de-

creasing strengths of 1–3 interactions. We performed MMP2 calculations on large delocalized cationic π -systems to determine the dominating effect. Table III lists nonbonded resonance stabilization energies of linear *all-trans* polyenyl cations ${}^+\text{CH}_2-(\text{CH}=\text{CH})_n-\text{H}$ depending on chain length n , and Figure 5 illustrates the results.

Nonbonded resonance stabilization energies increase up to a chain length of 13 carbons. A maximum π -stabilization effect of 14.9 kcal/mol has been found for π -systems with 11 and 13 carbons. Larger nonbonded resonance effects can only be found for cations with special geometric features like the 7-norbornenyl and homotropylium cations. The results for these cations are to be published. In larger π -systems, the strengths of 1–3 interactions decrease as a result of the lower π -charges centered on the individual carbons.

The decreasing strength of nonbonded resonance interactions with increasing chain length is the reason for the fact that resonance stabilization effects of vinyl groups in larger π -systems are lower than in neutral molecules.

Conclusions

The calculation of geometries and π -electron densities of delocalized cations by MMP2 and MP2(full)/6-31G* optimizations show that the results obtained by the two different methods agree well. Both methods compute an increasing delocalization of the charge and, consequently, decreasing strengths of hyperconjugation interactions with in-

TABLE III.
Resonance Energies, E_{res} , of a Terminal Vinyl Group of a Linear *All-Trans* Polyenyl Cation⁺
 $\text{CH}_2-(\text{CH}=\text{CH})_n-\text{H}$ Depending on π -Charge C_π of Terminal Carbon of Linear *All-Trans* Polyenyl Cation
 ${}^+\text{CH}_2-(\text{CH}=\text{CH})_{n-1}-\text{H}$ and Dependence of Nonbonded Resonance Stabilization Energy, E_{nobo} , in the
Former Cation on Chain Length n .

n	1	2	3	4	5
C_π	1.0	0.527	0.358	0.266	0.207
E_{res} (kcal / mol)	53.2	26.1	16.6	11.8	9.7
E_{nobo} (kcal / mol)	9.5	12.6	14.0	14.7	14.9
n	6	7	8	9	10
C_π	0.163	0.130	0.105	0.083	0.066
E_{res} (kcal / mol)	8.1	6.7	6.2	6.0	6.0
E_{nobo} (kcal / mol)	14.9	14.6	14.2	13.7	13.5
n	11	12	13	14	
E_{nobo} (kcal / mol)	13.1	12.8	11.8	11.2	

creasing magnitude of the π -system. The simple force-field method allows calculations of reasonable resonance energies in delocalized cations. The resonance energies of vinyl groups that stabilize a positive charge can be correlated with the stabilized charge and a linear dependence can be observed. The magnitude of the stabilization can be calculated approximately by MMP2. The simplicity of the force-field method, which allows a dissection of the energies into steric and electronic terms, and into σ - and π -energies, is the basis for the detailed analysis of electronic energies and effects.

A further advantage of MMP2 is the possibility of computing nonbonded resonance effects. The force-field calculations attach more importance to these interactions in cations than to neutral π -systems. The importance of these nonbonded resonance interactions increases with increasing chain length up to 13 carbons. For larger π -systems, the importance of nonbonded π -interactions decreases due to the decreasing π -charges centered on the

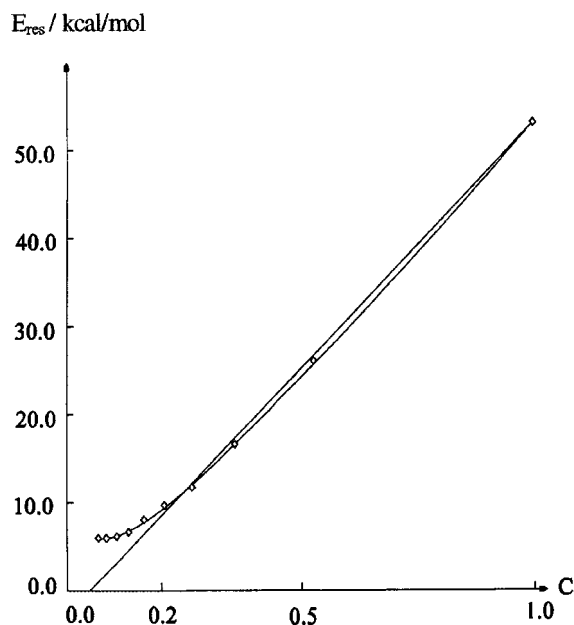


FIGURE 4. Dependence of the resonance energy, E_{res} , of a terminal vinyl group in the linear *all-trans* polyenyl cation $^+\text{CH}_2-(\text{CH}=\text{CH})_n-\text{H}$ on the π -charge C of the terminal carbon of the linear *all-trans* polyenyl cation $^+\text{CH}_2-(\text{CH}=\text{CH})_{n-1}-\text{H}$.

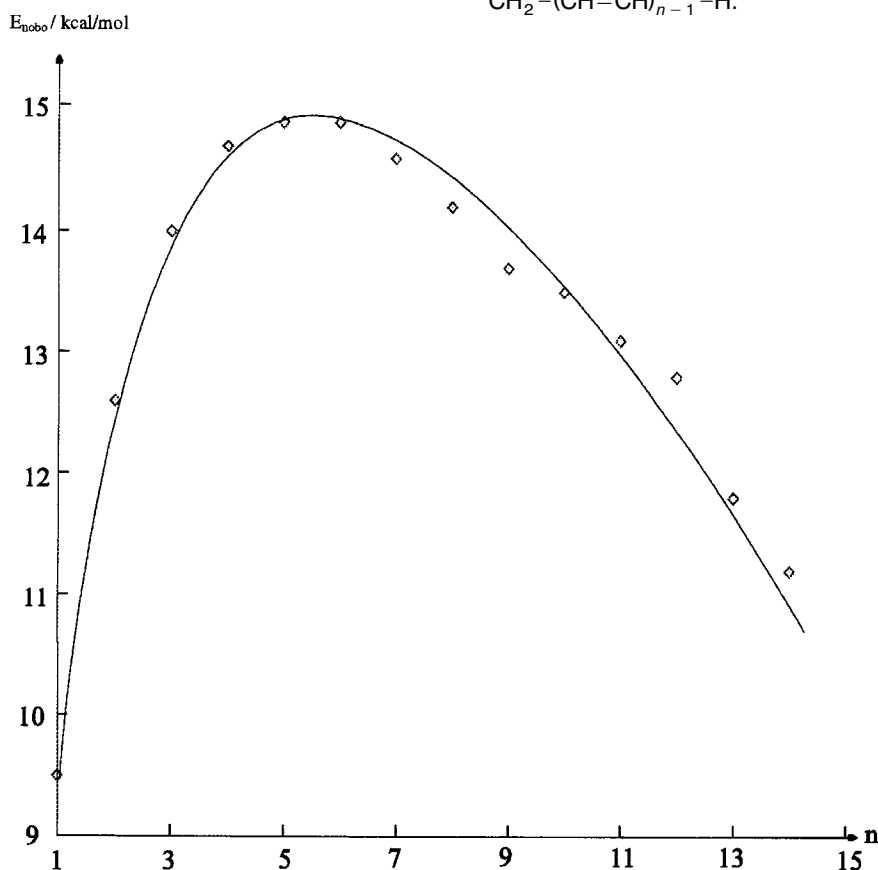


FIGURE 5. Dependence of nonbonded resonance stabilization energies, E_{nobo} , of linear *all-trans* polyenyl cations $^+\text{CH}_2-(\text{CH}=\text{CH})_n-$ on chain length n .

individual carbons. Another advantage of the force-field method is the possibility of optimizing large cations, which are currently out of the range for *ab initio* calculations on correlated levels.

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